

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 December 2003 (24.12.2003)

PCT

(10) International Publication Number  
**WO 03/106375 A1**

(51) International Patent Classification<sup>7</sup>: C04B 40/00,  
28/02, 22/12 // 103:10, 111:10

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(21) International Application Number: PCT/EP03/05456

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC,  
VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 22 May 2003 (22.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:

0213765.1 17 June 2002 (17.06.2002) GB  
0304158.9 25 February 2003 (25.02.2003) GB

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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WO 03/106375 A1

(54) Title: ACCELERATOR ADMIXTURE

(57) Abstract: An accelerator composition for use with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3 Component 1 - aluminium sulphate Component 2 - at least one of an alkanolamine and an alkylene diamine or triamine Component 3 - hydrofluoric acid optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present: Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate; Component 5 - C<sub>1</sub>- C<sub>10</sub> aliphatic mono- and dicarboxylic acids and their metal salts; Component 6 - aluminium hydroxide; Component 7 - at least one of phosphoric acid and phosphorous acid. The accelerators have excellent long-term stability and work well with "difficult" cements, such as some Japanese OPCs.

## ACCELERATOR ADMIXTURE

This invention relates to low alkali and alkali-free accelerators for sprayed cementitious compositions.

5

The use in cementitious compositions such as concrete to be applied by spraying of low alkali and alkali-free accelerators in place of the traditional aluminates and other strongly alkaline materials is now well established. The major components of such accelerators are aluminium compounds, the most commonly encountered being aluminium sulphate and

10 amorphous aluminium hydroxide. In addition to these aluminium compounds, a variety of other components have been used in such accelerators, these including alkanolamines, other aluminium salts (such as oxalates and nitrates) and various organic acids. More recent compositions have involved the use of fluoride ions.

15 The major problem in the art is to find an accelerator composition that combines acceptable performance, acceptable stability and an acceptable compressive strength. Stability can be a problem, especially in the more extreme conditions sometimes encountered in tunnels, and a reasonable shelf-life is necessary for a practical accelerator. All accelerators used in spraying concrete lower the compressive strength compared to the compressive strength of

20 the same concrete without accelerator. It is necessary that this lowering be kept to a minimum. In addition, a good early strength development in the 1-4 hour period after spraying is particularly desired.

In addition, the worldwide variation in cement types causes problems. What works well with

25 one cement in, say, Europe will not necessarily work so well with an Australian or a Japanese cement. It is difficult to formulate an accelerator that will work acceptably well with all types.

It has now been found that a particular combination of materials gives an accelerator that

30 performs especially well and is very stable. The invention therefore provides an accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate

Component 2 - at least one of an alkanolamine and an alkylene diamine or triamine

Component 3 - hydrofluoric acid

5 optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present;

Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate,

10 magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;

Component 5 - C<sub>1</sub> - C<sub>10</sub> aliphatic mono- and dicarboxylic acids and their metal salts;

Component 6 - aluminium hydroxide;

Component 7 - at least one of phosphoric acid and phosphorous acid

15

the ingredients being present in the following proportions (active ingredients by weight);

Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;

Component 2 - from 0.1 to 15%

20 Component 3 - from 0.2 to 8.0%

Component 4 - up to 15%

Component 5 - up to 15%

Component 6 - up to 15%

Component 7 - up to 5%.

25

Component 1, aluminium sulphate, may be any aluminium sulphate used in the manufacture of accelerators. It may be fully hydrated, or totally or partially calcined. A typical grade, and the one on which the proportion is based, is "17%" aluminium sulphate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.14.3H<sub>2</sub>O) (called thus because that is the proportion of aluminium oxide therein). should any other

30 aluminium sulphate be required, the appropriate quantity can be easily calculated on this basis. Preferably Component 1 is present in the proportion of from 30-46% by weight of the total accelerator composition.

Component 2, alkanolamine, alkylene diamine and alkylene triamine may be any such material, but is preferably ethylene diamine, ethylene triamine, diethanolamine or triethanolamine, most preferably diethanolamine. It is preferably present in the proportion of from 0.1- 10%, more preferably from 0.1 -8%, by weight of the total accelerator  
5 composition. It is possible to use a combination of two or more of such materials.

Component 3, hydrofluoric acid is generally used as an aqueous solution of about 40% HF by weight. The proportion of hydrofluoric acid present in the total accelerator composition (as HF) is preferably from 2-6%, more preferably from 2-4%, by weight of the total  
10 accelerator.

Component 4 may be selected from among the materials previously named. Although sodium and potassium are alkali metals, the proportion of such metals in the accelerator compositions according to this invention may be sufficiently low to permit these accelerators  
15 to be considered as alkali-free according to the accepted European definition (lower than 1% (weight) of Na<sub>2</sub>O equivalent). Up to 8.5% Na<sub>2</sub>O equivalent is considered "low alkali" and is acceptable for many purposes – in many cases, rigorous exclusion of alkali on health and environmental grounds is not necessary and a small proportion of at least one alkali metal enhances the early strength development. Thus, for the purposes of this invention, and  
20 contrary to the current practices of the art with respect to alkali-free accelerators, it is preferred that a minor proportion of alkali metal be present. This proportion is preferably no higher than 5% Na<sub>2</sub>O equivalent. The preferred proportion of Component 4 is from 1-10% by weight of the total accelerator composition. Component 4 is typically added to the accelerator composition as a 30% weight solution in water.

25

Component 5 may be selected from one or more of the group of acids. Especially preferred are formic, oxalic and glycolic acids and their metal salts, but other acids, such as acetic, propionic, succinic, citric and tartaric acids are also useful. Preferred proportions of Component 5 are from 2 - 10%, more preferably from 4 - 8%, by weight of the total  
30 accelerator composition.

It is required that at least one of Component 4 and Component 5 be present in the composition. The preferred Components 4 and/or 5 for the purposes of this invention are sodium oxalate, potassium oxalate and mixtures of one or both of these with lithium hydroxide. The LiOH/sodium-potassium oxalate mixtures are particularly preferred.

5

Component 6, aluminium hydroxide, is preferably amorphous aluminium hydroxide of the type normally used in accelerators for sprayed concrete. It is preferably present in the proportion of up to 10% by weight of the total accelerator composition. It is possible to use crystalline aluminium hydroxide; this is considerably cheaper, but it is difficult to dissolve

10 and it does not perform as well as the amorphous material.

Component 7, phosphoric acid ( $H_3PO_4$ ) or phosphorous acid ( $H_3PO_3$ ), acts as a stabiliser. Although it is possible to omit it, it confers a useful degree of stability on the accelerator compositions of this invention, a vital consideration in tunnelling operations where the  
15 accelerator may have to remain in a ready-to-use state for long periods. It is therefore preferably present, and in a concentration of from 0.1- 2% by weight of the accelerator composition. It is possible to use a blend of both acids, but it is preferred to use phosphoric acid alone.

20 The accelerator compositions may be prepared by simply mixing the abovementioned components in any order and stirring to give an aqueous solution. In some cases, additional water will need to be added. The final composition will generally comprise from 40-70% by weight of water.

25 Given the nature of the ingredients, the resulting accelerator composition will not be a simple mixture of ingredients but a complex blend of reaction products. For example, the HF will react with some other components (most especially aluminium hydroxide, if any be present). This composition is very stable, having a shelf life under normal storage conditions of several months.

30

In use, the accelerator composition of the invention is injected at a spray nozzle in the conventional manner. The dose is typically from 5 – 12% by weight accelerator composition

based on cement weight. The invention also provides a method of applying a cementitious composition to a substrate by spraying, comprising the steps of mixing a batch of fluid cementitious composition and conveying it to a spray nozzle, there being injected at the nozzle an accelerator as hereinabove described.

5

Sprayed cementitious compositions that utilise accelerator compositions according to this invention exhibit an unusually rapid build-up of compressive strength. In addition, the accelerator compositions work well with an unusually wide variety of cements, including Japanese cements, with which other alkali-free accelerators give less satisfactory results. The 10 invention also provides a hardened cementitious layer applied to a substrate by spraying through a spray nozzle, there having been added at the nozzle an accelerator as hereinabove described.

The invention is further illustrated by the following non-limiting examples in which all parts 15 are by weight.

A number of accelerators are added to a test mortar mix having the following constitution:

water	198 parts
20 ordinary Portland cement	450 "
sand (DIN 196-1)	1350 "
superplasticiser	2.7 "

The cement is Tayheiyo OPC, a commonly-used Japanese cement. The superplasticiser used 25 is NT-1000 ex NMB Ltd., Japan.

#### Example 1

To the abovementioned mix is added with thorough mixing 31.5 parts of an accelerator 30 according to the invention and having the following composition (given as percentages by weight):

## 6

aluminium sulphate (16H <sub>2</sub> O)	35
diethanolamine	2.1
sodium sulphate	11.2
oxalic acid	7.5
5 hydrofluoric acid	6
amorphous aluminium hydroxide	9.5
water	to 100%

## Example 2

10

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA162.

## 15 Example 3

Example 1 is repeated, with the exception that the 31.5 parts of the accelerator according to the invention is replaced by a commercially-available alkali-free accelerator sold as MEYCO® SA170.

20

The samples are tested for compressive strength according to prEN (preliminary European Standard) 12394 and the results obtained are shown below:

<u>Example No.</u>	Compressive strength		
	(MPa) at	6h	1d
1	3.6	20.1	39
2	1.4	1.8	23.2
3	0.8	8.6	28.9

30

It can be seen that the composition comprising the accelerator according to the invention develops compressive strength earlier than the compositions comprising the commercial accelerators, and that the final strength is substantially higher.

## CLAIMS:

1. An accelerator composition adapted to be used with sprayed cementitious compositions, which is an aqueous solution or dispersion of a blend of the essential Components 1-3:

Component 1 - aluminium sulphate  
Component 2- at least one of an alkanolamine and an alkylene diamine or triamine  
10 Component 3 - hydrofluoric acid

optionally with at least one of Components 4-7, with the proviso that at least one of Component 4 or Component 5 be present:

15 Component 4 - at least one of sodium hydroxide, potassium hydroxide, lithium hydroxide, magnesium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, sodium sulphate, potassium sulphate, magnesium sulphate and lithium sulphate;  
Component 5 - C<sub>1</sub> – C<sub>10</sub> aliphatic mono- and dicarboxylic acids and their metal salts;  
20 Component 6 - aluminium hydroxide;  
Component 7 - at least one of phosphoric acid and phosphorous acid.

the ingredients being present in the following proportions (active ingredients by weight);

25 Component 1 - from 30 to 60%, calculated on the basis of 17% aluminium sulphate;  
Component 2 - from 0.1 to 15%  
Component 3 - from 0.2 to 8.0%  
Component 4 - up to 15%  
30 Component 5 - up to 15%  
Component 6 - up to 15%  
Component 7 - up to 5%.

2. An accelerator according to claim 1, in which Component 4 is present.
3. An accelerator according to claim 2, in which Component 4 contains alkali metal to  
5 the extent of from 1-8.5% Na<sub>2</sub>O equivalent.
4. An accelerator according to claim 3, in which the alkali metal equivalent is 5% Na<sub>2</sub>O  
equivalent maximum.

10 5. A method of applying a cementitious composition to a substrate by spraying,  
comprising the steps of mixing a batch of fluid cementitious composition and  
conveying it to a spray nozzle, there being injected at the nozzle an accelerator  
according to claim 1.

15 6. A hardened cementitious layer applied to a substrate by spraying through a spray  
nozzle, there having been added at the nozzle an accelerator according to claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/05456

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C04B40/00 C04B28/02 C04B22/12 //C04B103:10, C04B111:10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 167 317 A (SIKA AG) 2 January 2002 (2002-01-02) paragraphs '0004!-'0040! example 1	1-6
Y	-----	2-4
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 03, 31 March 1999 (1999-03-31) & JP 10 330139 A (CHICHIBU ONODA CEMENT CORP;ONODA CO), 15 December 1998 (1998-12-15) abstract paragraphs '0001!-'0018! tables 2-4	2-4
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

26 August 2003

Date of mailing of the International search report

09/09/2003

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 03/05456

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 021158 A (CHICHIBU ONODA CEMENT CORP;ONODA CO; OHBAYASHI CORP), 26 January 1999 (1999-01-26) abstract paragraphs '0001!-'0013! table 4 ---	2-4
A	EP 1 167 315 A (SIKA AG) 2 January 2002 (2002-01-02) paragraphs '0004!-'0041! example 1 ---	1,5,6
A	WO 01 42165 A (HOFMANN THOMAS ;MBT HOLDING AG (CH)) 14 June 2001 (2001-06-14) page 1, line 21 -page 3, line 22 examples 1-5 ---	1,5,6
A	WO 98 18740 A (LUNKENHEIMER RUDOLF ;SEDELIES REINHOLD (DE); ALTMANN HORST (DE); B) 7 May 1998 (1998-05-07) page 2, line 11 -page 3, line 29 ---	2-4
A	EP 0 657 398 A (SIKA AG) 14 June 1995 (1995-06-14) page 2, line 14 -page 7, line 35 example 10 -----	

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/EP 03/05456

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 1167317	A	02-01-2002		EP 1167317 A1 AU 5188301 A CA 2349796 A1 JP 2002080250 A NZ 512250 A US 2002035952 A1		02-01-2002 03-01-2002 21-12-2001 19-03-2002 26-11-2002 28-03-2002
JP 10330139	A	15-12-1998		NONE		
JP 11021158	A	26-01-1999		NONE		
EP 1167315	A	02-01-2002		EP 1167315 A1 AU 5188201 A CA 2349997 A1 JP 2002029801 A NZ 512249 A US 2002023574 A1		02-01-2002 03-01-2002 21-12-2001 29-01-2002 26-11-2002 28-02-2002
WO 0142165	A	14-06-2001		AT 240913 T AU 2671901 A BR 0016261 A CA 2393458 A1 CN 1407954 T DE 60002918 D1 WO 0142165 A2 EP 1237827 A2 HU 0204379 A2 JP 2003516303 T NO 20022662 A NZ 519441 A SK 9772002 A3 US 2002195026 A1		15-06-2003 18-06-2001 20-08-2002 14-06-2001 02-04-2003 26-06-2003 14-06-2001 11-09-2002 28-06-2003 13-05-2003 08-08-2002 30-05-2003 04-03-2003 26-12-2002
WO 9818740	A	07-05-1998		WO 9818740 A1 AT 196453 T CA 2271629 C CZ 9901399 A3 DE 59605932 D1 DK 946451 T3 EP 0946451 A1 FI 990920 A GR 3035038 T3 JP 2001509124 T KR 2000052720 A NO 991769 A PL 332831 A1 SK 51599 A3 US 6302954 B1		07-05-1998 15-10-2000 25-03-2003 17-11-1999 26-10-2000 13-11-2000 06-10-1999 23-04-1999 30-03-2001 10-07-2001 25-08-2000 14-04-1999 11-10-1999 10-12-1999 16-10-2001
EP 0657398	A	14-06-1995		CH 686513 A5 AT 153010 T CA 2137309 A1 DE 69403183 D1 DE 69403183 T2 DK 657398 T3 EP 0657398 A1 ES 2102757 T3 GR 3024213 T3		15-04-1996 15-05-1997 07-06-1995 19-06-1997 09-10-1997 15-12-1997 14-06-1995 01-08-1997 31-10-1997

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/EP 03/05456

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0657398	A	JP	2930529 B2	03-08-1999
		JP	8048553 A	20-02-1996
		NO	944681 A	07-06-1995
		US	5560774 A	01-10-1996